MARK -1 , A CHEMICAL PROCESS TO DECOMPOSE WATER USING NUCLEAR HEAT

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INTRODUCTION

The evolution of nuclear reactors has followed mainly two trends:
1) The increase of the maximum coolant temperature
2) The decrease in the heat cost due to the progress in technology and to the increase in reactor size.

The demand for higher outlet temperatures, in view of higher efficiencies in the electric energy production, led to development of reactors capable of those high temperatures, e.g. the Advanced Gas Cooled Reactors, the Molten Salt Reactors, the High Temperature Gas Reactors. HTGR's have the advantage over the other two reactor concepts that their output coolant temperature is higher and that the properties of their core materials could tolerate additional increases in temperature.

Also from the commercial point of view the HTGR's won a round against to the other two with the order of Philadelphia Electric for a station equipped with two such reactors, with a total net electrical capacity of 2,320 Mwe. (1)

Electricity, the usual form for marketing nuclear energy, meets only about 20% of the energy needs for a technologically developed society. This fact limits the role nuclear energy can play in the total energy supply.

Looking for a mean to penetrate the remaining 80% of the energy market we considered that hydrogen could be the ideal carrier; so, a few years ago we started looking for a process to produce H_2 using nuclear heat.

The temperature level at which heat is available from the present family of HTGR's is such that it can be used in hydrogen production processes like coal gasification or natural gas reforming. In fact, there is a strong incentive for implementing those endothermic processes with nuclear heat because the difference in price between the fossil fuel calorie and the nuclear calorie is not negligible and tends to increase. But their thermodynamics is such that only 20-25% of the energy in the product comes from the nuclear reactor. The impact of such applications on the penetration of nuclear energy into the energy market will then be necessarily small. For this reason our research was oriented towards a process for hydrogen production in which the only energy input was from a nuclear reactor. In a sense water electrolysis (2, 3) works this way, but the necessary transformations through various stages of all the primary energy from heat to electricity and then, via electrolytic cells, to hydrogen, lead to low total efficiency and high investment cost.

We thought that a more direct use of heat could lead to higher conversion efficiencies and lower capital cost and we did set our goal at decomposing water using the nuclear heat for operating some endothermic chemical reactions in a closed cycle, i.e. with nominal consumption of chemicals.

THE CHEMICAL CYCLES

Thermodinamically it is not possible to crack water, with a reasonable yield, at temperatures lower than 2500°-3000°C. If we had to run

a process with only one endothermic reaction at a lower temperature we should compensate the lower entropical level of the heat by a corresponding amount of useful work. A multistep chemical process operating at different temperatures behaves as a thermal engine(4); as a consequence the useful work requirement can be obtained through extra heat entering the system at high temperature and given off as degraded heat at low temperature in accordance with the Carnot rule.

By a two-step process it is possible theoretically to split water even with a limit of 300°C for the upper temperature, but the thermodynamic properties of the chemical substances that could be used in such a cycle are very far from the thermodynamic properties of all known substances and following (4) even at 1000°C very probably such substances do not exist nor can they be synthesized.

Three-step processes appear more feasible and in fact they have been already proposed (5). They are based on the reaction of chlorine with steam at high temperature to produce oxygen and hydrochloric acid; the last-one being dissociated into hydrogen and chlorine by a reaction at low temperature with a low-valence metal chloride (metals being Ta, Bi, Hg, V) and the subsequent dissociation of the so formed high-valence chloride at high temperature.
The reactions for this type of a cycle are :

1) $Cl_2 + H_2O \longrightarrow 2HCl + 1/2\ O_2$

2) $2HCl + 2MeCl_2 \longrightarrow 2MeCl_3 + H_2$

3) $2\ MeCl_3 \longrightarrow 2\ MeCl_2 + Cl_2$

the reaction 1) and 3) run at high temperature and reaction 2) at low temperature.
Some experimental work has been done on the most promising cycle: the one employing Vanadium (6). The reaction between chlorine and steam has been tried to find the reaction rate as a function of temperature; reagents feed rate and ratio and reactor's surface-to-volume. The conditions for a pratical application have been found.

Some exploratory tests have been done about the reaction between vanadium dichloride and hydrochloric acid in a static-type apparatus at atmospheric pressure and at room temperature. In spite of the favourable reaction thermodynamics essentially no reaction between VCl_2 and HCl was observed in those conditions.

Another three-step process is described in U.S. Patent (1970)(7) in which Cesium metal reacts with water, then Cesium hydroxide is transformed into Cesium peroxide and finally Cesium peroxide is dissociated at high temperature. The reactions of this cycle are :

1) $2Cs + 2H_2O \longrightarrow 2\ CsOH + H_2$ at 100°C

2) $2CsOH + 3/2\ O_2 \longrightarrow 2\ CsO_2 + H_2O$ at 500°C

3a) $2CsO_2 \longrightarrow Cs_2O + 3/2\ O_2$ at 700°C

3b) $Cs_2O \longrightarrow 2Cs + 1/2\ O_2$ at 1200°C

No experimental work is reported in the patent description. With the available thermodynamic data we calculate for the reaction 2) quite an unfavourable equilibrium constant: H_2O partial pressure reaches only about one thousandth of the oxygen pressure. As a consequence, apart from the high upper temperature (about 1250°C), this process

requires quite an amount of separation work.

MARK-1 CYCLE

A four-step chemical cycle has been found by one of us (G.D.) (9) and it is briefly described in (8). This cycle, christened MARK-1, uses compounds of mercury, bromine and calcium. The set of reaction in the cycle is the following :

1) $CaBr_2 + 2H_2O \xrightarrow{730°} Ca(OH)_2 + 2HBr$ water splitting

2) $Hg + 2HBr \xrightarrow{250°} HgBr_2 + H_2$ hydrogen switch

3) $HgBr_2 + Ca(OH)_2 \xrightarrow{200°} CaBr_2 + HgO + H_2O$ oxygen shift

4) $HgO \xrightarrow{600°} Hg + 1/2\ O_2$ oxygen switch

Whose sum is :

$$H_2O \longrightarrow H_2 + 1/2\ O_2$$

A block diagram of the cycle is shown in fig. 1 where only materials flow is indicated.

In block 1) where reaction 1 occurs, calcium bromide and (excess) steam reacts to hydrobromic acid and calcium hydroxide. The hydrobromic acid solution is concentrated in a distillation column and fed to the step 2 (reaction n. 2). The product is a mixture of mercury bromides, hydrogen, hydrobromic acid, water and mercury. The gases are separated and hydrogen is cleaned from HBr traces by passing it through a bed of calcium hydroxide. Mercury and mercurous bromide, which is quite insoluble, are separated from the residual solution. Their mixture is fed back to step 2); the remaining solution is stripped to separate most of the hydrobromic acid and fed back into the distillation column at the proper level; the mercuric bromide solution is fed into step 3) with water and calcium hydroxide coming from step 1). The product of reaction 3 is a solution of calcium bromide easily separated from the mercuric oxide precipitate. The solution is concentrated and recycled to step 1). Mercury oxide is fed to step 4) where is dissociated. The products can be separated by quenching in an heat exchanger or by expanding them through a turbine. Mercury is recycled to step 2).

At this point the cycle is completed; the global result is an input of water and an output of hydrogen and oxygen. In fig. 2 a schematic flow-sheet for the Mark-1 process is given with reference

c) all by-products formed during the reactions can be reinjected at some points in the cycle, permitting a virtual 100% recuperation of the chemicals.

There are also some drawbacks :

a) the use of mercury with the related problems of high inventory cost and the possibility of pollution in case of leakages,

b) the use of highly corrosive chemicals, especially hydrobromic acid, and the consequent problems for construction materials.

CHEMICAL STUDIES (10)

Very little information on the reactions involved in the Mark-1 cycle was found in the literature. We then started a program of experimental tests in order to determine equilibria and kinetics.

1) On the hydrolysis reaction there is a paper (11) which describes a series of experiments in which various salts, like halides, sulphates, phosphates and carbonates of alkaline earth were hydrolized. The tests were performed in such a way that they did not allow the determination of equilibrium values for the hydrolysis; however they show that in the halide's family the most hydrolisable salt is calcium bromide. Our experiments on the hydrolysis of calcium bromide were done using water vapor at 1 atm. In order to have a preliminary idea of the equilibrium concentrations, thermodynamic calculations were made for the following reactions:

$$Ca\,Br_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + 2\,HBr$$

$$Ca\,Br_2 + H_2O \longrightarrow CaO + 2\,HBr$$

Working with steam at 1 atm. we can expect the formation of calcium hydroxide for temperature up to 550°C and the formation of calcium oxide at higher temperatures. Using for calculations the data of Brewer (12) and of Bulletin of Bureau of Mines (13) the values for the equilibrium constant range from 8.10^{-10} at 500°K to $1.07.10^{-4}$ at 1000°K; taking more recent data from Kubaschewski (14) these values are still lower, ranging from $1.2.10^{-12}$ at 500°K to $3.5.10^{-6}$ at 1000°K.
From our tests we find for the equilibrium constant values ranging from $2.9.10^{-7}$ at 573°K to $1.12.10^{-2}$ at 1000°K.
In fig. 3 there is a plot of calculated and experimental values for hydrolysis equilibrium constant at atmospheric pressure. Other tests are in progress to determine the equilibrium and the kinetics under pressure. A first test with 20 atm. steam led to an equilibrium constant of $1.9.10^{-2}$ at 727°C (1000°K).
The minimum working pressure necessary to have $Ca(OH)_2$ as product has been determined measuring the decomposition pressure of calcium hydroxide up to 800°C (fig. 4).

2) Also for the reaction between mercury and hydrobromic acid there is no valuable information in the literature. We did run a series of tests to determine how the reaction rate is influenced by the volume of hydrobromic acid, the surface of mercury, the tempera-

ture, the concentration of the acid.
Reacting a mercury drop of 550 mg (2.75 milli-atoms) in a glass vessel of about 35 ml volume with an excess of concentrate hydrobromic acid (48%, 8,9 milli-moles) at 250°C the initial rate of H_2 formation is 218 cc (NTP)/h.cm^2 of mercury. The initial vapor pressure of the hydrobromic acid has been evaluated to be 20 atm. From the reaction rates at temperatures between 197°C and 250°C the activation energy for the reaction has been calculated to be about 15 Kcal/mole. The temperature dependence of rate constant is shown in fig. 5. Extrapolating the reaction rate at 300°C we can expect a hydrogen formation rate of about 700 cc (NTP)/h.cm^2.
The influence of hydrobromic acid concentration on hydrogen formation rate at 200°C is given in fig. 6. It is quite evident the strong effect of the hydrobromic acid concentration.
Due to the overpotential for hydrogen evolution over mercury surfaces we have tested the effectivness of some metals as depolarisers. At 200°C the best results have been obtained with addition of iridium black on tungsten powder: hydrogen evolution rate did increase by a factor 2,3. At 250°C the effect of the catalyst is less important.
We are doing also some research on a different way to react mercury and hydrobromic acid. By the new procedure the reaction could be realized at lower temperatures (100 ÷ 120°C) with an acceptable rate. The lower temperature allows lower grade heat coming from other steps of the process to be used, and this permits a higher total efficiency. Analytical problems that did arise in the determination of the reaction products have been solved and the analytical procedure is described by Serrini (15).

3) About the reaction of mercury bromide with calcium hydroxide no information is available in the literature. Preliminary tests have shown that with calcium hydroxide, a brown colored precipitate is obtained. After boiling the solution for some minutes this brown precipitate is transformed in the usual red mercuric oxide. Nevertheless, a certain amount of mercuric bromide is held in solution by the calcium bromide formed. For this reason we began to study the influence of temperature, initial concentration of mercuric bromide and the excess of calcium hydroxide.

4) The dissociation of mercuric oxide is the only step of the Mark-1 cycle for which data are available in the literature.
Dissociation pressures have been measured (16) and are known with a precision sufficient for our needs. In fig. 7 HgO dissociation pressure versus temperature is given. Between 450°C and 600°C the dissociation pressure varies from 1 to 20 atm, that is in a range well suitable for pratical applications.
From the literature (17) it is also known that the rate of dissociation can be accelerated by the presence of a proper catalyst in the form of finely divided platinum, ferric oxide, etc.
As we need to know also the rate of recombination of oxygen and mercury vapors in order to define how fast the vapors must be cooled to avoid excessive back-reaction we are also studying the kinetic of HgO formation. In a very simple test, conducted by heating the mercuric oxide to 480°C at room pressure in a glass apparatus without any particular feature to cool the vapors, we did not observe any recombination. We are now assembling an apparatus

to study the recombination at temperatures up to 650°C and pressures up to 30 atm.

A list of other chemical and physical problems are under scrutiny e.g. we are measuring the vapor pressure of concentrated calcium bromide solutions, the heat of dehydratation of calcium bromide and the pressures and phase composition for the liquid-vapor equilibrium in the ternary system H_2O-HBr-$HgBr_2$.

We are also testing the reliability of specific ion-electrodes for continuous concentration measurements.

STRUCTURAL MATERIALS

The chemicals circulating in the various steps of the process are hydrobromic acid (vapors and solution), mercury (salts and vapor), calcium bromide and calcium hydroxide as solids and in solution, oxygen, hydrogen and water. For most of them compatible materials are known.

Problems arise with hydrobromic acid. For this product little information is available, and indication of its ability to attack material is derived from the behaviour of hydrochloric acid.
Corrosion conditions can be divided in two groups :

a) hydrobromic acid in solution

b) hydrobromic acid as gas mixed with steam.

Solutions of hydrobromic acid are formed :

a) where the steam and HBr mixture leaving the hydrolysis step is condensed; concentration will be about 33% by weight and at a temperature around 280°C;

b) in the concentration and stripping columns : temperature from 250°C down to 130°C and concentrations up to 48% by weigth (azeotropic);

c) where mercury is reacted, (concentration 48% by weigth, temperature 200°C).

The presence of mercury salts in the solution must be taken in account. Hydrobromic acid as a gas phase is present, mixed with steam, at a maximum concentration of 10% in volume (corresponding to a 33% in weigth) in the hydrolysis step and during the cooling of the mixture; a vapor phase is also present over the acid solution.

Exploratory corrosion tests (for metallic and refractory materials) have again begun in hydrobromic acid solutions (48%). After some screening at the boiling point of the azeotropic mixture (126°C) medium term tests with the most resisting materials have been done at 200°C and 250°C. The materials eliminated in the preliminary screening are : Chlorimet-2, Hastelloy B, Durichlor, Titanium, Vanadium, Nimonic 90, Stainless Steel AISI 304, Nickel, Chromium, Iron. We have retained : Tantalum, Molibdenum, Zirconium-Niobium alloy, Zircaloy-2 and Niobium. All testshave been done in glass capsules, with an external compensating pressure when necessary. The results are summarized in the following tables :

Test temperature 200°C

Material	Depth of attack in μ		
	100 hours	500 hours	1000 hours
Tantalum	nil	nil	nil
Molibdenum	≤1	≤1	≃1
Zr 2,5% Nb alloy	≤1	≤1	≤1
Zircaloy 2	≤1	≤1	≃1
Niobium	100	---	---

Test temperature 250°C

Material	Depth of attack in μ			
	100 hours	500 hours	1000 hours	1500 hours
Tantalum	nil	≤1	≤1	≤1
Molibdenum	≤1	≃2	≃5	≃6
Zr 2,5% Nb alloy	≃3	≃3	≃4	≃7
Zircaloy 2	≃3	≃9	≃12	≃14

COUPLING WITH THE HTGR

The cycle Mark-1 draws heat at different temperatures, the maximum temperature being 730°C. These quantities can be plotted in a diagram, with the temperature in °C as ordinate, and the quantity of heat (Kcal/mole H_2) as abscissa.
We can draw in the same diagram a similar plot for the heat carrier, and the distance between these lines will represents the ΔT in the heat exchangers. The amounts of heat represented by these lines are indexed according to the flow-sheet of fig. 2 and to the detailed portion of it as in fig. 8. We can see in fig. 9 how the heat quantities Q_{12} , Q_{11} , Q_{40} , Q_{34} and Q_{33} fit in the diagram. The heating fluid is represented with dotted lines. The figures refer to the production of 1 mole of H_2.

With the initial temperature of the fluid at 850°C and a minimum ΔT of 40°C we obtain the line a), with a mass-flow corresponding to a heat capacity of 540 cal/deg.C.

If we put in parallel, as it is shown in figures 2 and 9, the heat exchangers 11 and 12 we obtain line b). It is seen how the splitting of the heat carrier in two streams in the high temperature region permits a lower final temperature for the heat carrier. This is also the temperature of re-entry into the reactor, which is fairly critical due to the material problems it involves for the base of the reactor core.

Another possibility is that of bleeding part of the heat carrier and diverting it to make electricity. (fig. 9, line c). In both cases we have the possibility of producing mechanical or electrical energy for operating the auxiliaries of the plant and of the reactor.

A fixed critical point is the temperature of the hydrolysis reaction, taken as 730°C; lowering this temperature corresponds to an unacceptably low concentration of the hydrobromic acid produced in the reaction. On the contrary, the temperature levels of the heat blocks Q_{40} , Q_{34} , Q_{32} , can be shifted by a certain amount with respect to the values given above; the consequence of these shifts will be the variation of the pressure in some chemical steps.

These modifications may be useful for a better matching, between the heating fluid line and the Q lines, with a final lower mass-flow rate. For instance if we could raise the temperature of the reactor coolant to 900°C we could envisage a countercurrent series arrangement for the hydrolysis reaction, as it appears in fig.10 , and a lowering of 50°C, from 600°C to 550°C, of the heat block Q_{40} permits the coupling indicated in fig. 11. It is evident that the slope of the dotted line is quite higher : the mass-flow is now reduced to 230 cal/deg. C and the final coolant temperature is as low as 290°C, even without bleeding.

Our heat carrier can be the primary coolant of the nuclear reactor, e.g. helium. But in order to reduce the possibility of contamination we thougth it would be better to transfer the heat from the primary coolant of the reactor to an intermediate heat carrier (helium or better steam) by a heat exchanger installed in the reactor vessel. The long term objective is the use of steam both as an energy carrier and as a chemical, eliminating all the intermediate heat exchangers.

A very interesting point is that most of the heat produced by the nuclear reactor is correctly utilized in the chemical plant, so that the system is inherently a single-purpose one.

The plant rejects the degraded heat (around 50% of the input) in the form of saturated steam at 120-130°C. Expanding this steam through a turbine and condensing it permits the production of a seizable amount of electricity to be used in the plant, expecially to run the blowers of the reactor. It might eventually be used for a desalination plant or for a heavy water plant.

ECONOMIC CONSIDERATIONS

A precise economic evaluation of the cost of the hydrogen produced by the Mark-1 process is not possible with the informations available now on the yields and on kinetics of the various reactions or the kind of materials necessary for the apparatus.

Nevertheless it is possible to fix the frame in which the process has to fit to be competitive.

E.g. we can calculate the "room for investment", that is the maximum amount of capital that can be invested in the hypothesis of a hydrogen price competitive with the hydrogen produces today by steam-reforming of natural gas. To find this we parametrise a certain number of technological data :

a) the cost of nuclear calorie

The cost of the nuclear heat produced by an HTGR of about 3,000 Mwth is usually indicated to be in the order at 1 mil/Mcal (18). We'll take a range between 0.75 to 1.25 mils/Mcal.

b) the thermal efficiency of the chemical process

This efficiency can be defined as the ratio between H_2 combustion

heat and the primary heat necessary to produce it.
Such definition is somehow equivocal because the heat of combustion can be assumed to include or not the condensation of the water produced, and because waste heat is released from the process as steam at temperatures still interesting for the production of electricity.

E.g. with the heat rejected from blocks 14, 22 and 23 (fig.2) by a plant equipped with the 3,000 Mwth reactor, it would be possible to operate low-pressure steam turbines for 100 ÷ 150 Mwe. The fraction of this electricity not used inside the plant should be properly discounted from the primary heat budget.

With the heat source at 750°C, the heat sink at 25°C, and operating the water decomposition process in a reversible way, with materials (water, hydrogen and oxygen) entering and leaving the process at 25°C and 1 atm, the thermodynamical efficiency is $\sim$ 0.85 Funk (4). The temperature of 25°C means that water is liquid, i.e. that the higher value for the combustion heat of H_2 (3,000 Kcal/Nm^3) is taken. For our efficiency evaluations we usually assume the lower combustion heat (2,500 Kcal/Nm^3), and we find actual efficiencies in the order of 0.4 - 0.6. This is the range chosen for this parameter. Electricity production is neglected.

c) the oxygen credit

The european mean price for oxygen is around $ 6/ton; for our calculations a maximum credit of $ 4/ton is taken, corresponding to 2.9 mils/Nm^3H_2.

d) heavy water credit

By contacting the incoming water with the outgoing hydrogen in an isotopic exchange column, Deuterium can be trapped in the H_2 plant, e.g. at a factor of ten enrichment, and bled to a finishing plant. With current prices for D_2O we have evaluated a net D_2O credit of $\sim$ 3 mils/Nm^3H_2 (Market value of the D_2O produced is around 7 mils/Nm^3H_2.

Credits (c) and (d) can be very important in establishing the profitability of the first plants. The learning curve for the process should later take care of the diminishing value that can be allocated to these by-products, once the market will be swamped.

Fig. 12 gives the room for investment as a function of these parameters taking 12 mils/Nm^3 as the reference price for the hydrogen. E.g. with the nuclear calorie at 1 mil/Mcal; a thermal efficiency of 0.5 and an oxygen credit of $ 4/ton we have 9.9 mils/Nm^3H_2 available for fixed costs. In a conventional steam reforming plant fixed costs are around 4 mils/Nm^3H_2.

The sensivity of the hydrogen price in relation to these parameters is indicated in fig. 13, where the reference point assumes: fixed costs 6 mils/Nm^3, thermal efficiency 0.5, cost of the nuclear heat 1 mil/Mcal and oxygen credit $ 2/ton.

As the cost of our hydrogen is almost purely technological(uranium cost enters for less than 1 mil/Nm^3H_2 and can be less than 0.1 mils/Nm^3H_2 in the case of breeders), there is no rock-bottom cost, and the cost will decrease exponentially as a function of the integrated amount produced, according to a general rule valid for all the mass produced chemicals (19). This means that if we can achieve competivity in the chemical hydrogen market, it is only a question of time to become competive in the energy market. This because the

cost of minerals in general and fuels in particular tends to slowly rise with time.

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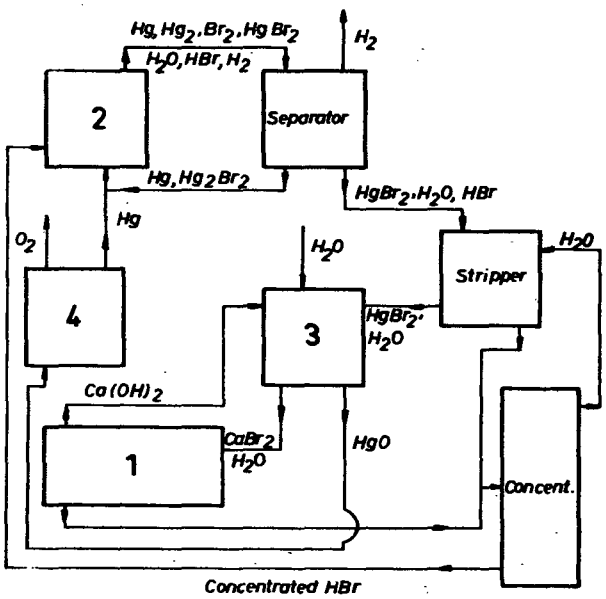

FIG. 1 Mark-1 block diagram

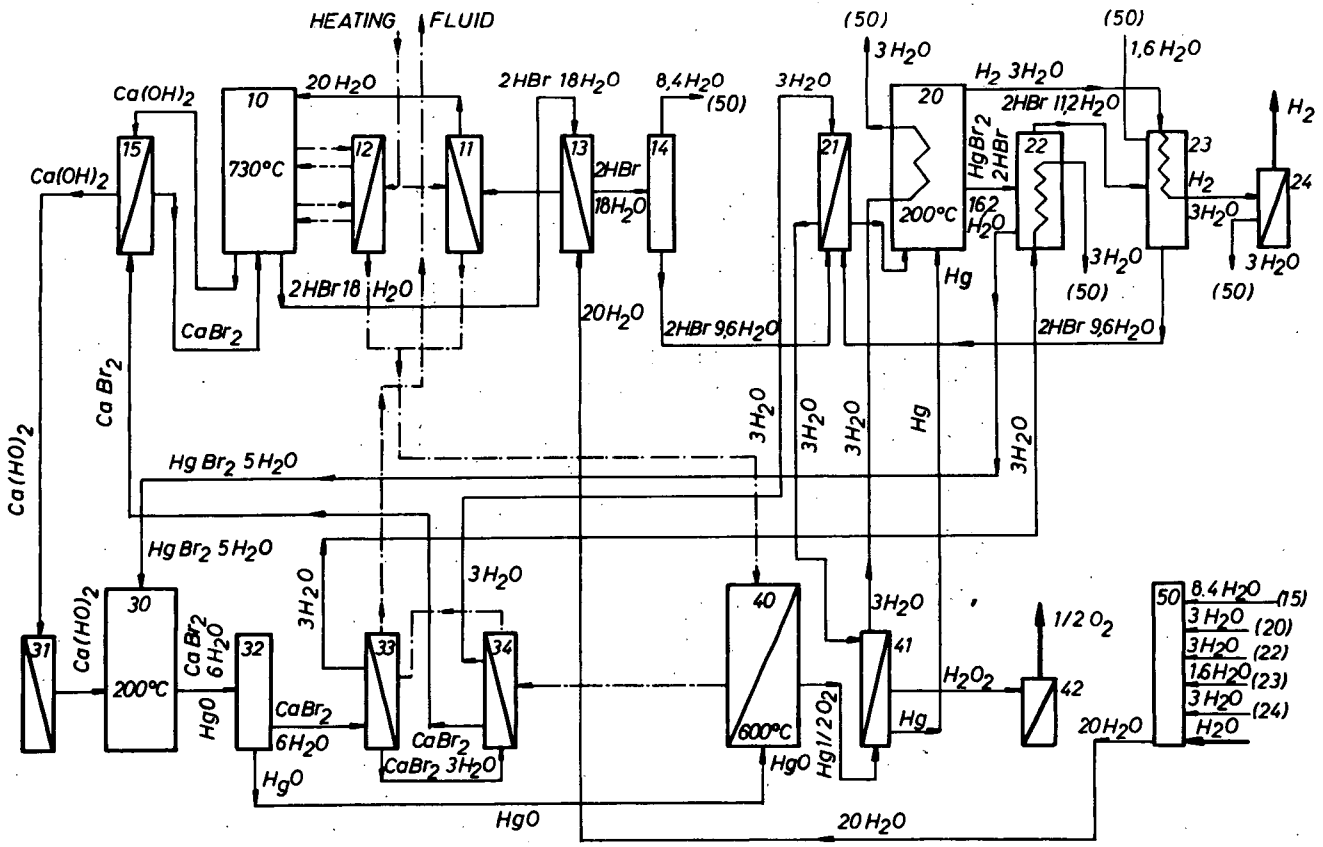

FIG. 2 Simplified flow-sheet showing materials flow and temperatures

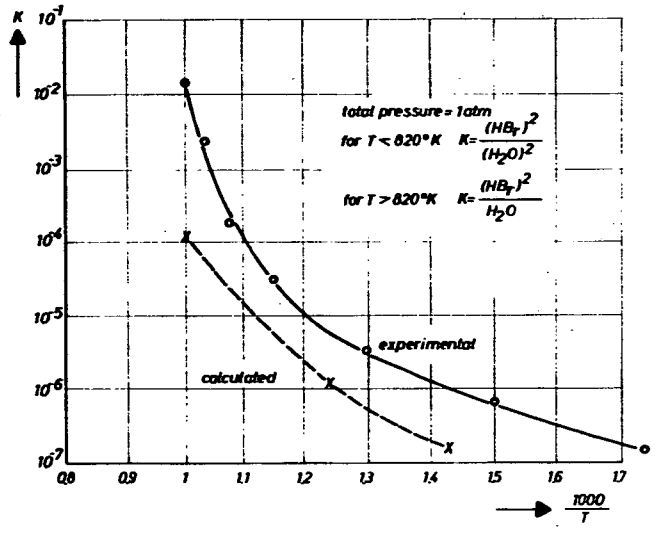

FIG.3 Hydrolysis equilibrium constants as a function of temperature

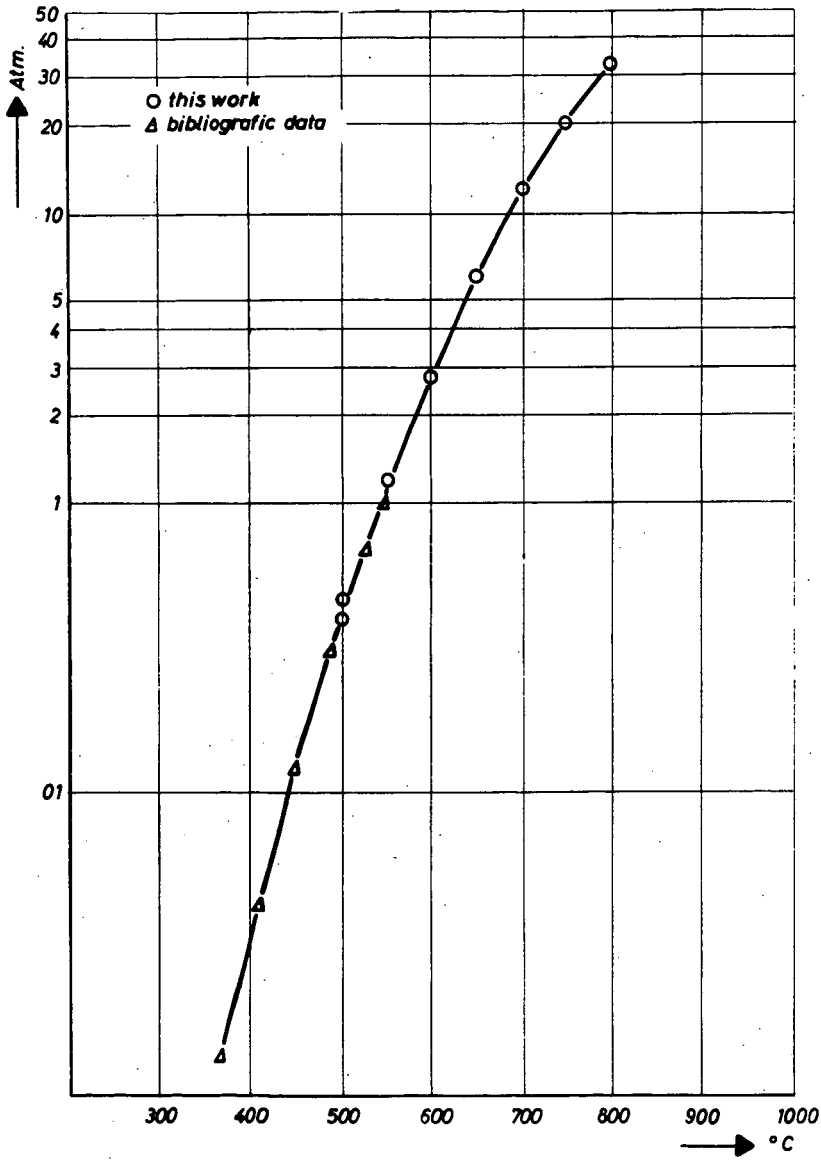

FIG. 4 $Ca(OH)_2 \longrightarrow CaO + H_2O$ Decomposition pressures

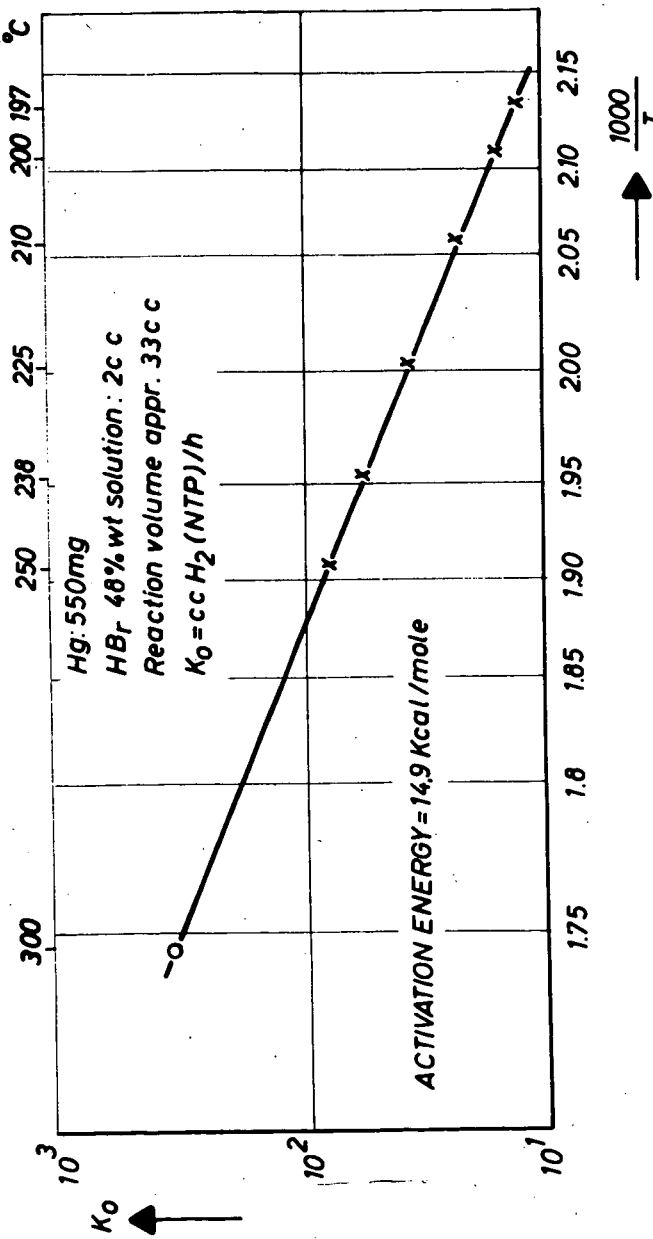

FIG. 5 $Hg + 2HBr \rightarrow HgBr_2 + H_2$ Temperature dependence of rate constant.

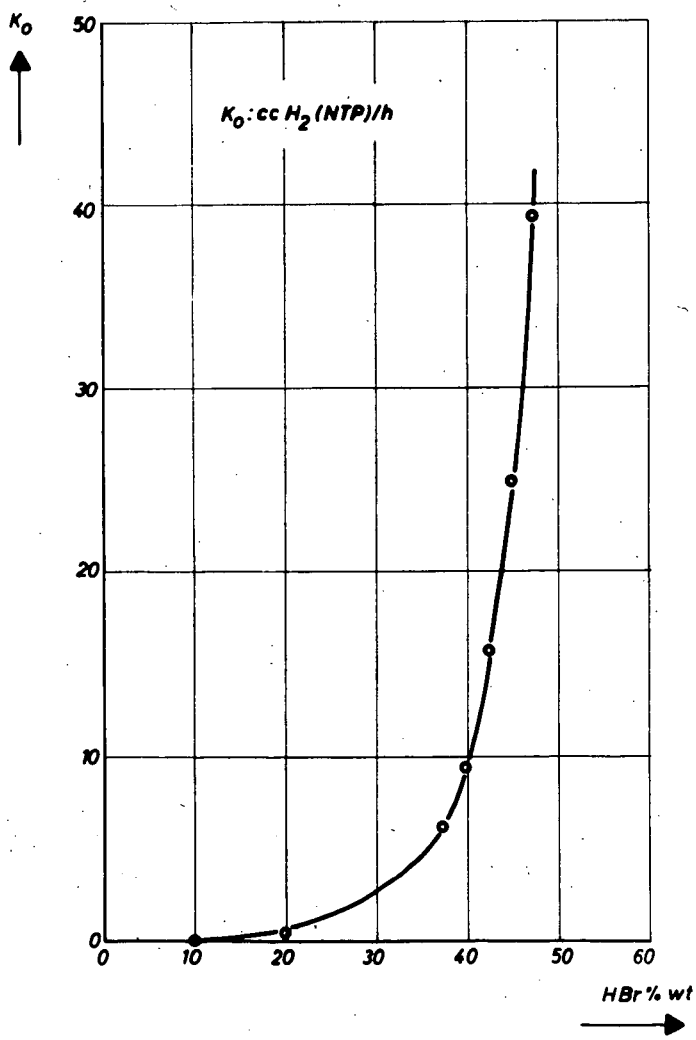

FIG. 6 $Hg+2HBr \rightarrow HgBr_2+H_2$ Hydrogen formation rate at 200°C influence of HBr concentration

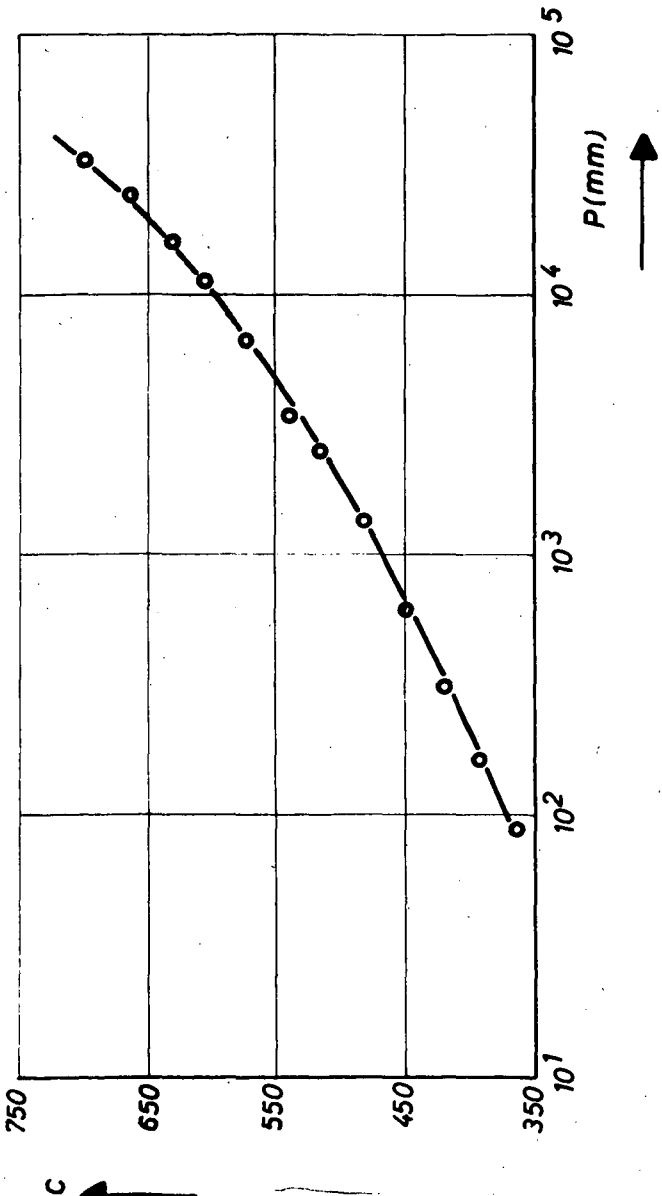

FIG. 7 $HgO \rightarrow Hg + \frac{1}{2} O_2$ Dissociation pressures

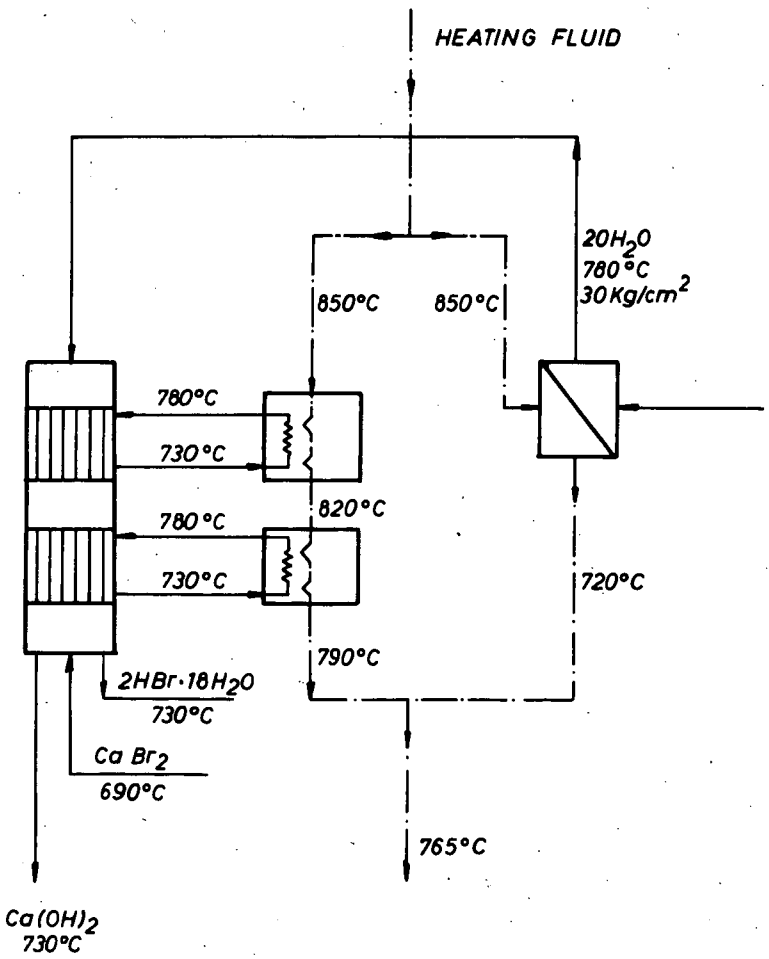

FIG. 8 Mark-1 flow-Sheet- Detail of the hydrolysis step

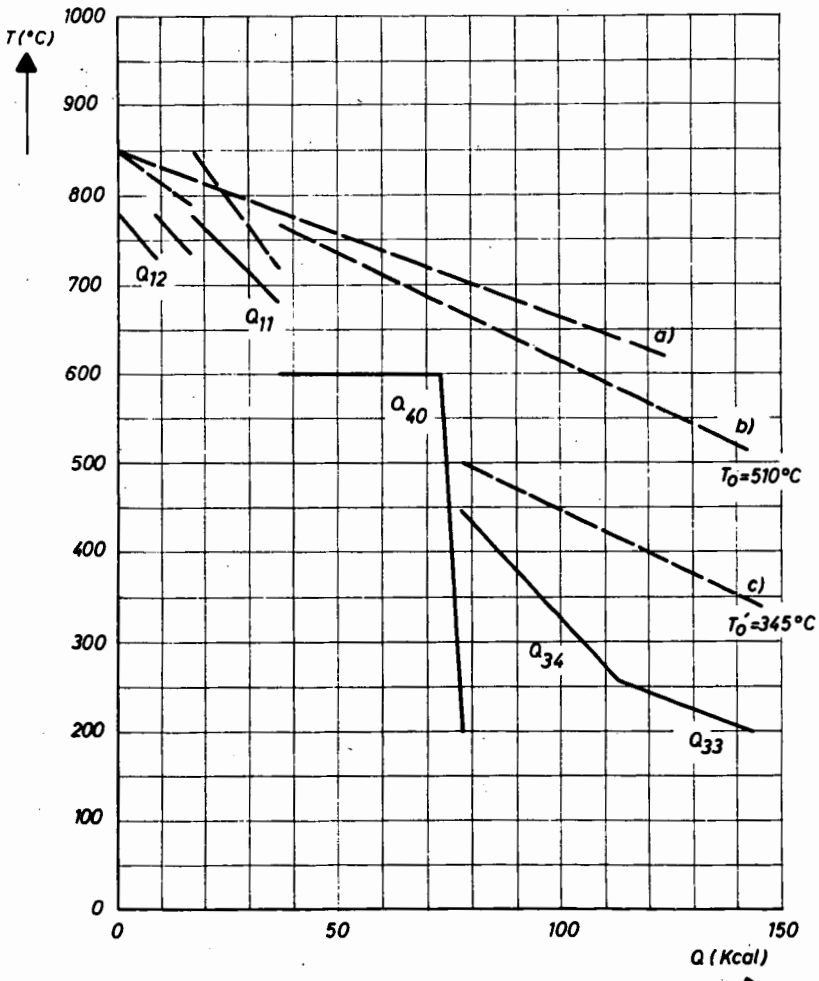

FIG. 9 Example of process thermal coupling using 850°C helium gas as primary heat carrier

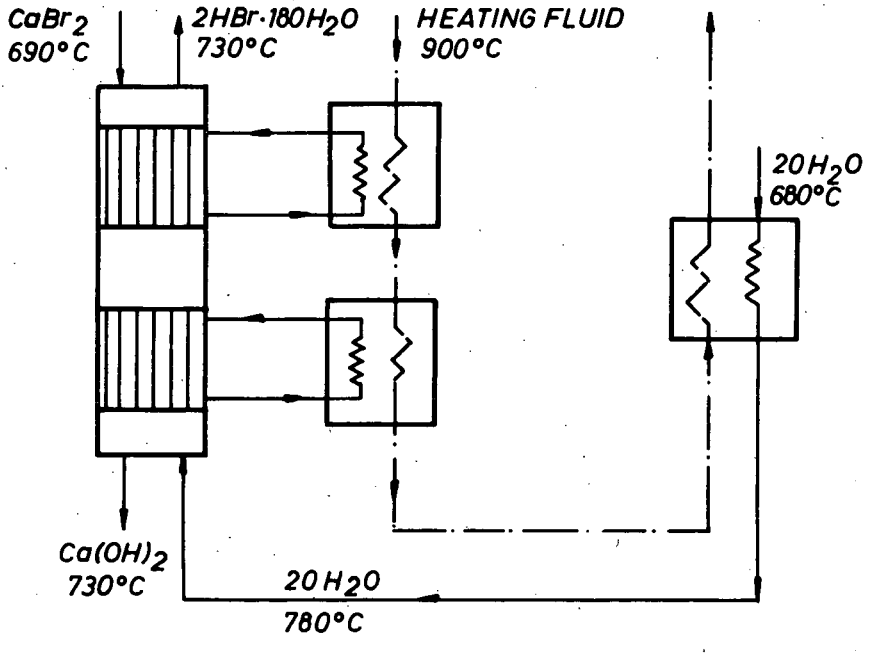

FIG.10 Mark-1 flow sheet countercurrent scheme for the hydrolysis step

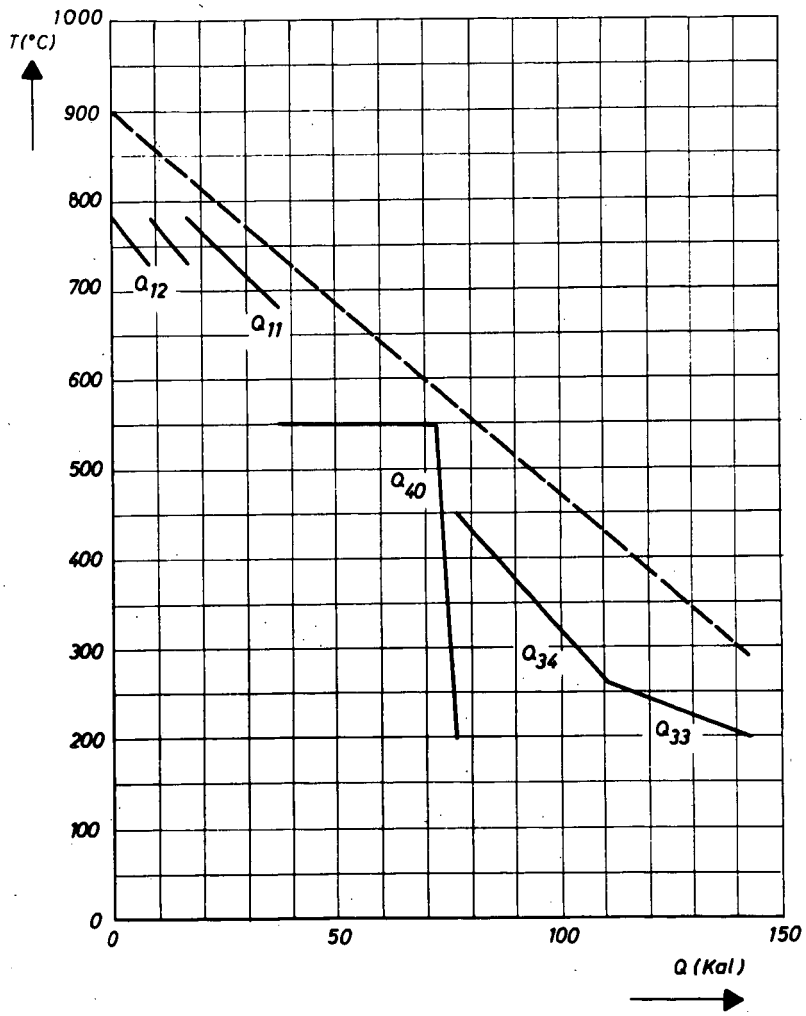

FIG.11 Example of process thermal coupling using 900°C helium gas as primary heat carrier

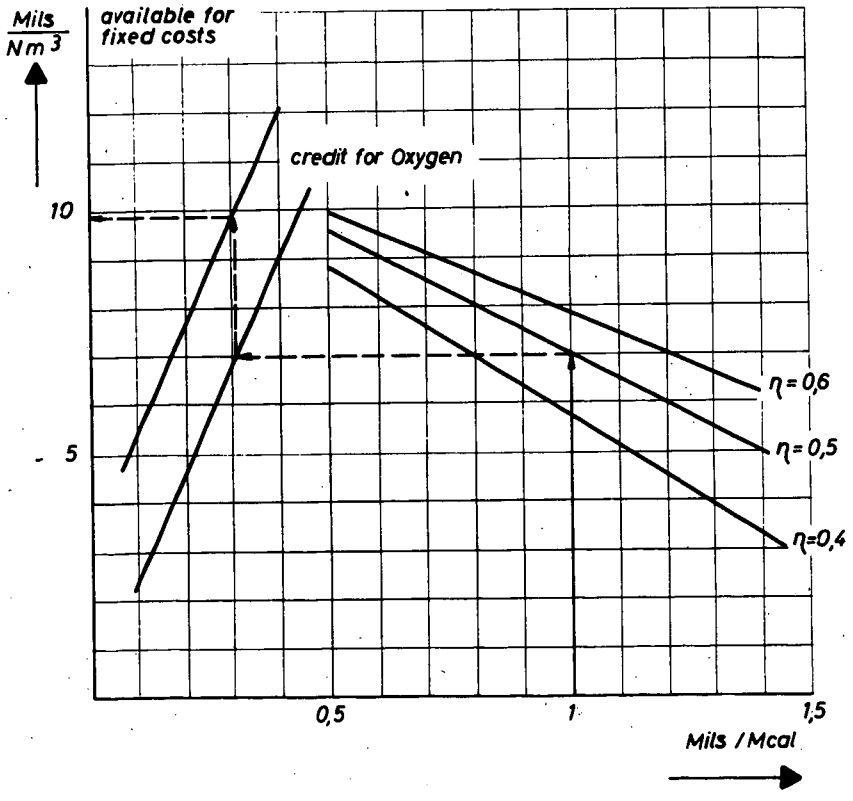

FIG. 12 Abacus for fixed costs evaluation

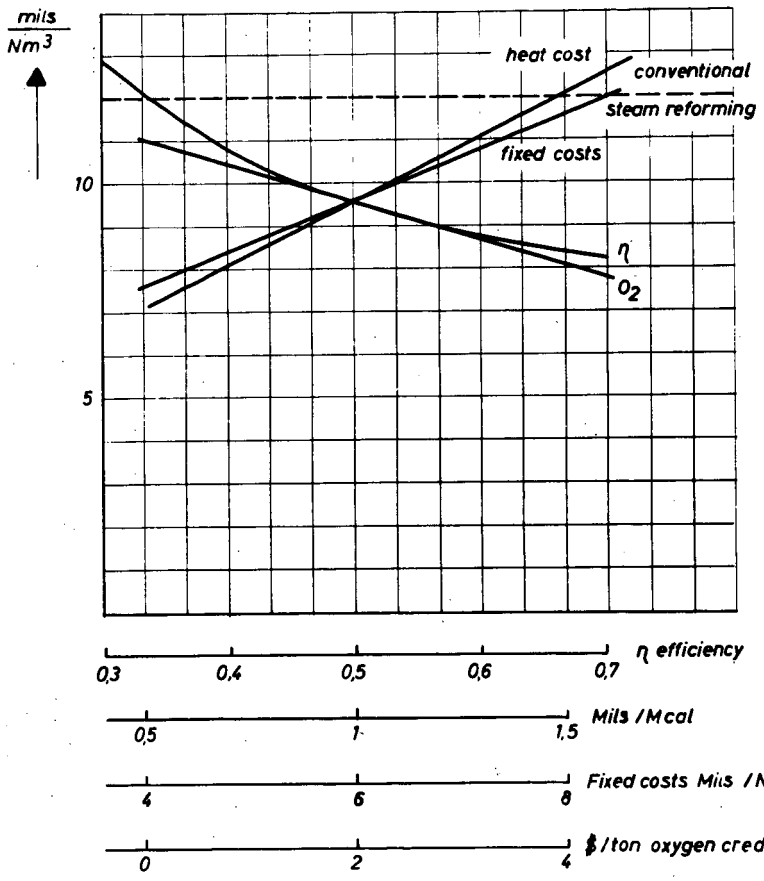

FIG.13 Hydrogen costs as a function of process efficiency, heat cost, fixed costs and oxygen credit